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Process for the desulphurization of an engine fuel onboard a motor vehicle

The invention relates to a process for the desulphurization of an engine fuel onboard a motor vehicle.

The desulphurization of engine fuel is usually carried out using large-scale chemical processes in refineries during production of the fuel. Processes which are known for this purpose include extraction, adsorption (e.g. US 5,360,536), distillation or microbiological processes. Commercially available engine fuels in Europe currently have a residual sulphur content of approximately 200 ppm. This causes problems with regard to the sulphur compatibility of modern exhaust-gas aftertreatment systems, which include adsorbers and catalytic converters. Therefore, residual sulphur contents of less than 10 ppm are desired.

It is an object of the invention to provide a process for separating off sulphur-containing components from an engine fuel which is suitable for use in mobile systems. In particular, only a small overall volume and a low weight should be required in order to implement this process.

This object is achieved by the process according to Claim 1. Advantageous embodiments of the invention form the subject matter of further claims.

According to the invention, the desulphurization of the fuel takes place onboard the motor vehicle by selectively separating off the sulphur-containing fuel components by means of liquid-phase adsorption. To do this, an adsorption material which selectively adsorbs

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substantially only the sulphur-containing fuel components is used.

The adsorption means used is in particular solids with a high surface area (in particular in the range from 10 to 1 600 m²/g), primarily substances of this type which contain Al, Mg, Si or Ti in oxide form. Examples of these MgO, SiO $_2$, TiO $_3$, are Al.O., substances hydrotalcites or mixed oxides. It is also possible to use the said substances doped with a metal, such as for example an alkali metal, an alkaline-earth metal, a rare earth, or Ag, Cu, Co, Fe, Mn, Ni, V or Zn. Biogenic materials, such as for example enzymes, can also be used. Furthermore, it is possible to convert the sulphur contained in the fuel into other sulphur compounds by means of microorganisms which are brought into contact with the fuel.

The adsorption material has a temporaly limited separating capacity and has to be replaced after a period of time as part of the regular servicing of the vehicle. In an alternative embodiment, however, the adsorption material can also be regenerated onboard the motor vehicle, in particular by heat treatment. The regeneration can advantageously be carried out by temperature control by means of the coolant circuit (approx. 80°C) or engine oil circuit (> 100°C) which is present in the vehicle.

In an advantageous embodiment, adsorption device and fuel filter can be integrated in a single structural unit. In this case, adsorption material and the material for the fuel filtering may, for example, be arranged or layered immediately next to or on top of one another.

By using the low-sulphur fuel obtained, it is possible to significantly prolong the service life of modern exhaust-gas after-treatment systems.

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The low-sulphur fuel is particularly suitable for being added when a spark-ignition engine is operating in lean-burn mode.

In the case of a diesel engine, the particle emissions in the exhaust gas can be reduced by the addition of low-sulphur diesel fuel.

In addition to being used as an engine fuel, the low-sulphur fuel can also be used as a reducing agent for deNOx catalytic converters in lean exhaust gas.

A further application for the low-sulphur fuel obtained using the process according to the invention is its use in the desulphurization of a catalytic converter in an exhaust-gas after-treatment system of an engine. In the exhaust-gas after-treatment system, from time to time sulphur accumulates on the surface of the catalytic converter and is removed by regeneration (desorption). This can only take place with low-sulphur exhaust gas.

The outlay on equipment for carrying out the process according to the invention is low. Consequently, it is also possible for the overall volume and weight to be kept low. The process according to the invention is therefore suitable for use in all mobile systems, such as passenger or commercial vehicles or in rail-borne vehicles.

A further advantage of the process according to the invention is that the low-sulphur fuel fraction is available onboard as soon as the engine is started. It is therefore possible to dispense with an additional storage tank for low-sulphur fuel specifically for the cold-start phase.

The low-sulphur fuel obtained can either be utilized immediately or can be stored in a tank.

The process according to the invention can be used for all engine fuels, in particular petrol or diesel fuels, kerosine or methanol.

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The invention is explained in more detail with reference to drawings, in which:

- shows a first structure for carrying out the process according to the invention;
- Fig. 2 shows a second structure for carrying out the 5 process according to the invention;
 - Fig. 3 shows an adsorption device for carrying out the process according to the invention;
- Fig. 4 shows a test structure for determining the adsorber properties and adsorber capacity; 10
 - Fig. 5 shows the effect of the fuel sulphur content on the NO_x conversion of an exhaust-gas aftertreatment system.

The adsorption device may be connected in series downstream of the fuel pump (Fig. 1) or as a bypass to 15 the normal fuel supply (Fig. 2) -

Fig. 1 shows an arrangement with the fuel pump and adsorption device arranged in series. The fuel is removed from the fuel tank KT by means of electrical fuel pump KP and then passes through the adsorption device AD according to the invention before being fed to the engine via the injection nozzle ED. The intake pipe of the denoted by AR. In the series circuit engine is illustrated here, all the fuel supplied to the engine is desulphurized.

In the case of the bypass circuit, it is possible switch between the normal branch, without adsorption device, and the branch with the adsorption device, by means of a valve V. In this way, it is possible to employ the desulphurization only in certain operating phases of the engine. For example, desulphurization can be included in a controlled manner only when the engine is in lean-burn mode and during desulphurization of the adsorber catalytic converter contained in the exhaust-gas after-treatment system. The

35 bypass circuit illustrated allows the running capacity of

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the adsorption device to be increased or allows the adsorption device to be of smaller design.

Fig. 3 diagrammatically depicts an adsorption device in the form of a separating column, the interior of which is filled by the adsorption material. The sulphur-containing fuel mixture to be separated is introduced undiluted into the inlet of the separating column and is passed to the adsorption material. The sulphur-containing fuel components are selectively adsorbed on the adsorption material. The sulphur-free (generally low-boiling) fuel components which have not been adsorbed leave the separation column at the opposite end as the eluate. The separation column is surrounded by an annular channel through which a heat-transfer medium flows in order to control the temperature of the separation column.

Fig. 4 shows the test structure for determining the adsorber properties and the adsorber capacity. The fuel is removed from a storage vessel and is passed through the temperature-controlled adsorption column by means of a HPLC pump (max. throughput 10 ml/min). For quantitative analysis, the eluate can be analysed offline by means of gas chromatography and X-ray fluorescence analysis.

Fig. 5 shows the effect of the sulphur content of the fuel on the NO $_{\rm x}$ conversion of an exhaust-gas after-treatment system. The operating duration (in hours) is plotted on the abscissa, and the NO $_{\rm x}$ conversion (in $^{\circ}$) is plotted on the ordinate. Two series of measurements were recorded for sulphur contents of 31 ppm and 130 ppm, with the same type of catalytic converter. The tests were carried out using a direct-injection spark-ignition engine in mixed lean-burn mode (30 seconds of lean-burn mode with λ = 1.5 and 2 seconds of rich-burn mode with λ = 0.75). As can be seen from the comparison of the

measurement series, the service life of the catalytic converter falls drastically with a high sulphur content.